

FILLED ELASTOMERIC BUTYL COMPOUNDS

FIELD OF THE INVENTION

The present invention relates to a rubber compound containing at least one solid, optionally halogenated, butyl elastomer and at least one nanoclay that have decreased die swell and mill shrinkage, improved 5 extrusion rates and hot air aging resistance. The present invention also related to a compound containing bromobutyl elastomers.

BACKGROUND OF THE INVENTION

It is known that reinforcing fillers such as carbon black and silica 10 greatly improve the strength and fatigue properties of elastomeric compounds. It is also known that chemical interaction occurs between the elastomer and the filler. For example, good interaction between carbon black and highly unsaturated elastomers such as polybutadiene (BR) and styrene butadiene copolymers (SBR) occurs because of the large number 15 of carbon-carbon double bonds present in these copolymers. Butyl elastomers may have only one tenth, or fewer, of the carbon-carbon double bonds found in BR or SBR, and compounds made from butyl elastomers are known to interact poorly with carbon black.

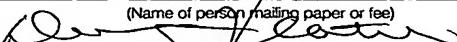
Nanoclays are processed nanometer-scale clays having 20 nanometer-thick platelets that can be modified to make the clay complexes compatible with organic monomers and polymers. Typically nanoclays are processed natural smectite clays, such as sodium or calcium montmorillonite, which have been the first choice for producing nanoclays, due to their availability, easy extraction, and relatively low cost. The 25 heterogeneity of natural clay can be a problem. This can be overcome by using synthetic clays such as hydrotalcite and laponite. They may or may not be organically treated to provide "gallery spacing" and to promote

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compatibility with the resin of choice. Most treatments include onium ion substitution reactions and/or the dipole moment modification.

- Nanoclays are expanding clays. The structure and chemical makeup of expanding clays means that individual platelets will separate
5 from each other to interact with some swelling agent, typically water.

Cloisite® nanoclays are produced by Southern Clay Products, Inc., of Texas, USA. They are high aspect ratio additives based on montmorillonite clay.

- PCT Patent Application WO-98/56598-A1 discloses barrier coating
10 mixtures contain in a carrier liquid (a) an elastomeric (preferably butyl-containing) polymer; (b) a dispersed exfoliated layered filler having an aspect ratio greater than 25; and (c) at least one surfactant, wherein the solids content of the mixture is less than 30 % and the ratio of polymer (a) to filler (b) is between 20:1 and 1:1. However, the present invention
15 teaches solid elastomeric polymers and does not require use of surfactants. The absence of water means that individual platelets will not necessarily separate from each other to interact with water instead of the polymer. Additionally, the use of solid polymers significantly decrease the cost of the manufacturing process.

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SUMMARY OF THE INVENTION

- The present invention provides a rubber compound containing at least one solid, optionally halogenated, butyl elastomer and at least one nanoclay. Those compounds have improved properties when compared
25 to known filled rubber compositions with respect to extrusion rates and decreased die swell and mill shrinkage.

- The present invention also provides rubber compounds containing at least one bromobutyl elastomer. The present invention also includes nanoclay is based on a smectite clay, such as a montmorillonite clay, or
30 for example commercially available clays, such as, Cloisite® nanoclays.

Accordingly, the present invention also provides a process which includes mixing at least one solid, optionally halogenated, butyl elastomer with at least one nanoclay, such as a nanoclay based on a smectite clay, for example, a montmorillonite clay, or, further for example, a Cloisite®
5 nanoclay, optionally in the presence of a curing system and/or further additives, extruding the compound and curing the resulting shaped filled, optionally halogenated, butyl elastomer. Further, the present invention also provides a curable compound, having improved processability and heat aging properties.

10

DETAILED DESCRIPTION OF THE INVENTION

The present invention will now be described for purposes of illustration and not limitation. Except in the operating examples, or where otherwise indicated, all numbers expressing quantities, percentages, and
15 so forth in the specification are to be understood as being modified in all instances by the term "about." Also, all ranges include any combination of the maximum and minimum points disclosed and include any intermediate ranges therein, which may or may not be specifically enumerated herein.

The phrase "halogenated butyl" or "halobutyl elastomer(s)" as used
20 herein refers to a chlorinated or brominated butyl elastomer. Brominated butyl elastomers are preferred, and the invention is illustrated, by way of example, with reference to such bromobutyl elastomers. It should be understood, however, that the invention extends to the use of non-halogenated or chlorinated butyl elastomers.

25 Thus, optionally halogenated, butyl elastomers suitable for use in the practice of this invention include, but are not limited to, brominated butyl elastomers. Such elastomers may be obtained by bromination of butyl rubber which is a copolymer of isobutylene and one or more co-monomers, usually a C₄ to C₆ conjugated diolefin, such as isoprene, alkyl-
30 substituted vinyl aromatic co-monomers such as C₁-C₄-alkyl substituted

styrene. An example of such an elastomer which is commercially available is brominated isobutylene methylstyrene copolymer (BIMS) in which the co-monomer is p-methylstyrene.

Brominated butyl elastomer typically contains from 1 to 3 weight percent of isoprene and from 97 to 99 weight percent of isobutylene (based upon the hydrocarbon content of the polymer) and from 1 to 4 weight percent bromine (based upon the bromobutyl polymer). A typical bromobutyl polymer has a molecular weight, expressed as the Mooney viscosity (ASTM D1646, ML 1 + 8 at 125°C), of from 28 to 55.

For use in the present invention the optionally brominated butyl elastomer contains in the range of from 1 to 5 weight percent of isoprene and from 95 to 99 weight percent of isobutylene (based upon the hydrocarbon content of the polymer) and from 0.5 to 2.5 weight percent, or for example from 0.75 to 2.3 weight percent, of bromine (if halogenated and based upon the brominated butyl polymer).

According to the present invention the optionally halogenated butyl elastomer can be the sole elastomer. If mixtures are to be used, however, then the other elastomer may be, for example, natural rubber, polybutadiene, styrene-butadiene or poly-chloroprene or an elastomer compound containing one or more of these elastomers.

Examples of suitable butyl elastomers include Bayer Butyl 100, Bayer Butyl 101-3, Bayer Butyl 301, and Bayer Butyl 402 commercially available from Bayer Inc. Bayer Butyl 301 has a Mooney viscosity (ML 1+8 @ 125°C) of 51 ± 5 MU, an residual double bond content of 1.85 mol% and an average molecular weight (Mw) of 550,000 grams per mole. Bayer Butyl 402 has a Mooney viscosity (ML 1+8 @ 125°C) of 33 ± 4 MU, an residual double bond content of 2.25 mol% and an average molecular weight (Mw) of 430,000 grams per mole.

Examples of suitable brominated butyl elastomers include Bayer Bromobutyl 2030, Bayer Bromobutyl 2040 (BB2040), and Bayer Bromobutyl X2 commercially available from Bayer Inc. Bayer BB2040

has a Mooney viscosity (ML 1+8 @ 125°C) of 39 ± 4 MU, a bromine content of 2.0 ± 0.3 wt% and an average molecular weight of 500,000 grams per mole.

- The present invention is not limited to a particular nanoclay. Thus,
- 5 any nanoclay known by the skilled in the art should be suitable. For example, natural powdered, optionally modified with organic modifiers, smectite clays, such as sodium or calcium montmorillonite, or synthetic clays such as hydrotalcite and laponite are useful in the present invention. Powdered montmorillonite clays that have been modified with organic
- 10 modifiers are also useful, such as montmorillonite clays modified with halogen salts of $(CH_3)_2N^+(HT)_2$, where HT is hydrogenated Tallow (~65% C₁₈; ~30% C₁₆; ~5% C₁₄) or $(CH_3)_2N^+(CH_2-C_6H_5)(HT)$, where HT is hydrogenated Tallow (~65% C₁₈; ~30% C₁₆; ~5% C₁₄). These clays are available as Cloisite® clays 10A, 20A, 6A, 15A, 30B, 25A.
- 15 The present inventive compound contains in the range from 0.01 to 10 phr (per hundred parts of rubber) of nanoclay(s), for example from 1-5 phr, or, for example from 2-4 phr of nanoclay(s).

- The present inventive compound may further contain at least one filler such as carbon black and/or mineral fillers such as silica, silicates,
- 20 clay (such as bentonite), gypsum, alumina, aluminum oxide, magnesium oxide, calcium oxide, titanium dioxide, talc and the like, as well as mixtures thereof.

- Useful mineral fillers have a mean agglomerate particle size between 1 and 100 microns, for example, between 10 and 50 microns or
- 25 for example, between 10 and 25 microns. It is preferred that less than 10 percent by volume of the agglomerate particles are below 5 microns or over 50 microns in size. A suitable amorphous dried silica moreover has a BET surface area, measured in accordance with DIN (Deutsche Industrie Norm 66131), of between 50 and 450 square meters per gram and a DBP
- 30 absorption, as measured in accordance with DIN 53601, of between 150 and 400 grams per 100 grams of silica, and a drying loss, as measured according to DIN ISO 787/1.1, of from 0 to 10 percent by weight. Suitable

silica fillers are available under the trademarks HiSil® 210, HiSil® 233 and HiSil 243 from PPG Industries Inc. Also suitable are Vulkasil S and Vulkasil N, from Bayer AG.

Useful carbon blacks are those prepared by the lamp black, furnace 5 black or gas black process and have BET (DIN 66 131) specific surface areas in the range of from 20 to 200 m²/g, e.g. SAF, ISAF, HAF, FEF or GPF carbon blacks.

The amount of filler to be incorporated into the present inventive 10 compound can vary between wide limits. The filler(s) can be present in an amount in the range from 20-200 phr, or for example, 50-150 phr. It may be advantageous to use a mixture of carbon black(s) and mineral filler(s).

The filled compound can be cured to obtain a product, which has improved properties, for instance in heat aging. Curing can be effected 15 with high-energy radiation or a curative, such as sulfur. The useful amount of sulfur is in the range from 0.3 to 2.0 phr (parts by weight per hundred parts of rubber). An activator, for example zinc oxide, may also be used, in an amount in the range of from 5 parts to 0.5 parts by weight. Other ingredients, for instance stearic acid, rosins (e.g. Pentalyn® of Hercules Inc., USA), oils (e.g. Sunpar® of Sunoco), antioxidants, or accelerators 20 (e.g. a sulfur compound such as dibenzothiazyldisulfide (e.g. Vulkacit® DM/C of Bayer AG) may also be added to the compound prior to curing. Sulphur curing is then effected in the known manner. See, for instance, chapter 2, "The Compounding and Vulcanization of Rubber", of "Rubber Technology", 3rd edition, published by Chapman & Hall, 1995, the 25 disclosure of which is incorporated by reference.

Other curatives known to cure halobutyl elastomers may also be used. A number of compounds are known to cure BIIR such as bis dieneophiles (for example HVA#2 = m-phenylene-bis-maleimide), phenolic resins, amines, amino-acids, peroxides, zinc oxide and the like.

30 Combinations of the aforementioned curatives may also be used.

A stabilizer may be added to the brominated butyl elastomer.

Suitable stabilizers include calcium stearate and epoxidized soybean oil, used in an amount in the range from 0.5 to 5 parts by weight per 100 parts by weight of the halogenated butyl rubber.

5 The optionally halogenated butyl elastomer, nanoclay, optionally
filler and additives are mixed together, suitably at a temperature in the
range of from 25 to 200°C. Or, the temperature in one of the mixing
stages may be greater than 60°C, or for example, a temperature in the
range from 90 to 150°C. Normally the mixing time does not exceed one
10 hour; a time in the range from 2 to 30 minutes is usually adequate. It is
advantageous to mix the butyl elastomer and nanoclay for at least
2 minutes before any other component is added. The mixing is suitably
carried out on a two-roll mill mixer, which provides good dispersion of the
filler within the elastomer. Mixing may also be carried out in a Banbury
15 mixer, or in a Haake or Brabender miniature internal mixer. An extruder
also provides good mixing, and has the further advantage that it permits
shorter mixing times. It is also possible to carry out the mixing in two or
more stages. Further, the mixing can be carried out in different
apparatuses, for example one stage may be carried out in an internal
20 mixer and another in an extruder.

The order of addition of the different components to the rubber masterbatch is not critical, however, it might be advantageous to add the curatives in the last mixing step to prevent unwanted preliminary cross-linking (scorch).

25 The combination of the optionally halogenated butyl elastomer(s)
with the nanoclay(s) results in improved properties for the filled
compounds. These improved properties include lower die swell, less mill
shrinkage, faster extrusion times and improved heat aging combined with
a lower Mooney scorch (scorch is the unwanted preliminary cross-linking
30 of the compound during handling). These render the cured compounds
particularly suitable for a number of applications including, but not limited

to, use in tire treads and tire sidewalls, tire innerliners, tank linings, hoses, rollers, conveyor belts, curing bladders, gas masks, pharmaceutical enclosures and gaskets.

The invention is further illustrated in the following examples.

5

EXAMPLES

Description of tests:

Cure rheometry:

10 Vulcanization was followed on a Moving Die Rheometer (MDR 2000(E)) using a frequency of oscillation of 1.7 Hz and a 3°arc at 166°C for 30 minutes total run time. The test procedure follows ASTM D-5289.

Compound Mooney Viscosity and Scorch.

15 A large rotor was used for these tests and ASTM method D-1646 was followed. The compound Mooney viscosity was determined at 100°C by preheating the sample 1 minute and then, measuring the torque (Mooney viscosity units) after 4 minutes of shearing action caused by the viscometer disk rotating at 2 r.p.m. Mooney scorch measurements taken as the time from the lowest torque value to a rise of 5 Mooney units (t05) 20 were carried out at 125°C.

Stress-strain.

25 Samples were prepared by curing a macro sheet at 166°C for 30 minutes, after which the appropriate sample was die cut into standard ASTM die C dumbbells. The test was conducted at 23°C and conforms to ASTM D-412 Method A.

Hot air aging/stress-strain:

30 Vulcanized dumbbell die C samples were aged for 168 hrs in a hot air oven at 120°C and then tested at 23°C. This test complies with ASTM D-573.

30 Hardness:

 All hardness measurements were carried out with an A-2 type durometer following ASTM D-2240 requirements

Mill Shrinkage.

This test complies with ASTM D-917, Method B. The test is performed at 50°C (roll temperature) for 70g of halobutyl sample.

5 ***Haake Extrusion with Garvey die: ¾" diameter screw and 10" screw length.***

The barrel temperature was set at 100°C while the Garvey die was at 105°C. The single screw was turning at 45 r.p.m. Testing was carried out according to ASTM D-2230.

10 **Description of Ingredients and General Mixing Procedure:**

Cloisite® 10A, 20A, 6A - Montmorillonite – organically modified - products of Southern Clays

Cloisite® NA+ - Montmorillonite – not organically modified - a product of Southern Clays

15 Bayer Bromobutyl 2030 – brominated butyl by Bayer Inc.

Sunpar® 2280 - paraffinic oil produced by Sun Oil.

Pentalyn® A –Synthetic Resin by Hercules, Inc.

Stearic acid Emersol 132 NF – stearic acid by Acme-Hardesty Co.

Carbon Black, N 660 – carbon black by Cabot Corp.

20 Vulkacit® DM/C – dibenzothiazyldisulfide (MBTS) by Bayer AG

Sulfur NBS - sulfur by N.I.F.T.

Kadox® 920 grade PC 216 – zinc oxide by St. Lawrence Chem. Inc.

25 The brominated butyl elastomer and the nanoclay were mixed in a 1.57 liter Banbury internal tangential mixture with the Mokon set to 30°C and a rotor speed of to 77 RPM for 2 minutes. Carbon black, Pentalyn®, stearic acid, Sunpar®, and Vulkacit® were then added to the compound and the compound was mixed for another 4 minutes. To the cooled sample, sulfur NBS and Kadox® was added on a 10" x 20" mill at 30°C

with the Mokon set to 30°C. Several three-quarter cuts were performed to homogenize the curatives into the masterbatch followed by six end-wise passes of the compound.

5 **Example 1**

Nine batches were prepared according to Table 1. Example 1a is a comparative example.

TABLE 1 Formulations

<u>Example</u>	1a/control	1b	1c	1d	1e	1f	1g	1h
<u>Nanoclay</u>	<u>none</u>	<u>Cloisite® NA+</u>	<u>Cloisite® 10A</u>	<u>Cloisite® 20A</u>	<u>Cloisite® 20A</u>	<u>Cloisite® 20A</u>	<u>Cloisite® 6A</u>	<u>Cloisite® 6A</u>
Nanoclay amount (phr)	0	2	2	4	2	4	2	4
Bayer® Bromobutyl 2030 (phr)	100	100	100	100	100	100	100	100
Carbon Black N 660 (phr)	60	60	60	60	60	60	60	60
Pentaly® A (phr)	4	4	4	4	4	4	4	4
Stearic acid (phr)	1	1	1	1	1	1	1	1
Sunpar® 2280	7	7	7	7	7	7	7	7
Vulkacit® DM/C	1.3	1.3	1.3	1.3	1.3	1.3	1.3	1.3
Sulfur NBS	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
Kadox® 920	3	3	3	3	3	3	3	3

TABLE 2 Moving Die Rheometer Results

<u>Example</u>	1a/control	1b	1c	1c	1e	1f	1g	1h
<u>Nanoclay</u>	<u>none</u>	<u>Cloisite® NA+</u>	<u>Cloisite® 10A</u>	<u>Cloisite® 20A</u>	<u>Cloisite® 20A</u>	<u>Cloisite® 20A</u>	<u>Cloisite® 6A</u>	<u>Cloisite® 6A</u>
Nanoclay amount (phr)	0	2	2	4	2	4	2	4
MH (dN.m)	17.58	16.41	22.53	19.09	20.05	22.33	21.11	24.04
ML (dN.m)	4.92	4.83	4.79	4.79	4.6	4.36	4.56	4.64
MH-ML (dH.m)	12.66	11.58	17.74	14.3	15.45	17.97	16.55	19.4
T _{s1} (min)	1.26	1.32	1.11	1.62	1.2	1.23	1.14	1.08
T ₅₀ (min)	2.53	2.65	3.58	4.04	3.33	4.08	3.5	4.51
T ₉₀ (min)	12.1	14.89	6.71	12.27	6.83	7.7	6.61	8.26

TABLE 3 Processing characteristics

Example	1a	control 1b	1c	1d	1e	1f	1g	1h
Nanoclay	none	Cloisite® NA+	Cloisite® 10A	Cloisite® 20A	Cloisite® 20A	Cloisite® 6A	Cloisite® 6A	Cloisite® 6A
Nanoclay amount (phr)	0	2	2	4	2	4	2	4
Compound Mooney scorch t05 (min)	22.45	24.93	28.3	>30	28.18	>30	>30	>30
ML (1+4@1100C) – (MU)	60.9	60.5	60.7	59.6	59.2	57.1	57.7	59
Haake Die Swell (%)	23.3	25.0	16.7	8.9	11.4	15.0	13.6	13.4
Haake Extrusion Rate (cm/m)	52	53	54	58	57	56	56	62
Mill Shrinkage (%)	20	17.3	16.7	15.3	16.7	12	16	12.7

TABLE 4 Stress Strain Initial Physical Properties

Example	1a	/control 1b	1c	1d	1e	1f	1g	1h
Nanoclay	none	Cloisite® NA+	Cloisite® 10A	Cloisite® 20A	Cloisite® 20A	Cloisite® 6A	Cloisite® 6A	Cloisite® 6A
Nanoclay amount (phr)	0	2	2	4	2	4	2	4
Hard Shore A2 Inst. (pts)	59	58	62	64	64	64	60	64
Ultimate Tensile (MPa)	10.66	10.64	10.8	9.36	10.85	11.04	11.1	11.35
Ultimate Elongation (%)	735	725	630	536	678	624	698	612
Stress – 25% (MPa)	0.65	0.64	0.73	0.69	0.72	0.79	0.71	0.76
Stress – 50% (MPa)	0.81	0.81	0.9	0.86	0.89	0.98	0.89	0.99
Stress – 100% (MPa)	1.11	1.16	1.32	1.23	1.26	1.44	1.3	1.5
Stress – 200% (MPa)	2.24	2.4	2.87	2.6	2.63	3.08	2.81	3.33
Stress – 300% (MPa)	3.9	4.16	5.02	4.65	4.66	5.3	4.85	5.7

TABLE 5 Stress Strain Hot air aged Property changes (168hrs at 120°C in hot air oven)

Example	1a/control	1b	1c	1d	1e	1f	1g	1h
<i>Nanoclay</i>	none	Cloisite® NA+	Cloisite® 10A	Cloisite® 10A	Cloisite® 20A	Cloisite® 20A	Cloisite® 6A	Cloisite® 6A
Nanoclay amount (phr)	0	2	2	4	2	4	2	4
Chg. Hard Shore A2 Inst. (pts)	6	7	-1	-2	-1	2	5	1
Chg. Ultimate Tensile (%)	-9	-15	-11	7	-6	-7	-9	-14
Chg. Ultimate Elongation (%)	-31	-37	-7	2	-16	-16	-22	-19
Chg. Stress - 25% (%)	40	48	11	17	31	25	32	37
Chg. Stress - 50% (%)	54	54	24	33	44	38	46	40
Chg. Stress - 100% (%)	97	77	44	56	71	59	71	52
Chg. Stress - 200% (%)	114	83	45	63	76	58	70	42
Chg. Stress - 300% (%)	80	59	25	40	48	36	45	23

The data in Table 2 clearly shows the effect of adding nanoclay to the brominated butyl elastomer batch, especially when compared to the control compound 1a. All maximum torque values increase upon clay addition (1c through 1h) showing an important reinforcing effect of the
5 nanoclays. It can be seen that organic modification of the nanoclays is important as the Cloisite Na⁺ does not provide additional reinforcement. At the same time, minimum torques values for compounds containing Cloisites 10A, 20A and 6A are slightly lower compared to both the control 1a and the Cloisite Na⁺ containing compound 1b. Lower minimum torques
10 are indicative of a better compound flow before the onset of vulcanization. Delta torque values are all larger in magnitude for compounds 1c – 1h compared to the control compound 1a and 1b and take into account the increased compound flow before vulcanization and the higher level of reinforcement caused by the nanoclays.

15 The data in Table 3 clearly shows the processing benefits of nanoclay addition to the brominated butyl elastomer batch compared to the control 1a and compound 1b. Compound Mooney Scorch is actually lengthened by at least 5 minutes by nanoclay addition. Clay addition addition would help prevent any prevulcanization that could take place
20 during moulding or extruding. Compound Mooney viscosities are slightly lower upon nanoclay addition (compounds 1d – 1h) with the biggest effects (5% reduction) seen with 4 phr of Cloisite 20A (compound 1f) and 2 phr of Cloisite 6A (compound 1g). Lower compound Mooney viscosities are indicative of better processing. Haake extrusion rates are quicker by
25 nanoclay addition with improvements of up to 19% compared to the control and compound 1b when 4 phr of Cloisite 6A is added to the bromobutyl masterbatch (compound 1h). Faster extrusion rates are advantageous for better increased overall production capabilities. Haake extrusion Garvey die swells are clearly improved upon nanoclay addition with a die swell
30 reduction of 35 to 62 % compared to both compounds 1a and 1b. 4 phr of Cloisite 6A addition provided the most die swell improvement. Die swell is undesirable during extrusion and any reduction of this phenomenon would

be beneficial to the process. The magnitude of mill shrinkage was also decreased by nanoclay addition. Improvements anywhere from 15 to 40% less mill shrinkage was observed. 4 phr of Cloisite 20A (compound 1f) provided the biggest reduction in compound mill shrinkage. A reduction in
5 mill shrinkage is important, for example, in tire building, especially when splicing is required between two compound ends.

Table 4 illustrates the effects of nanoclay addition in the bromobutyl masterbatch on initial physical properties. It is important to note the non-reinforcing effect of Cloisite Na⁺ in the bromobutyl masterbatch
10 (compound 1b) as for all intents and purposes, its initial physical properties are the same as the control compound. Nanoclay addition (Cloisites 10A, 20A and 6A) causes a slight hardening and stiffening of the compound as seen by the higher hardness and moduli values (compounds 1c – 1h). A small reduction in elongation is noted with very little effect seen on tensile
15 values.

The effect of nanoclay addition in the bromobutyl masterbatch on stress strain hot air aging is illustrated in table 5. It can be observed that nanoclay addition (compounds 1c – 1h) produces minimal changes in the hardness upon aging, preventing the hardening of the bromobutyl
20 compound. At the same time, lower change in stress values are seen in all nanoclay compounds compared to the control. Elongation changes are also lower in the nanoclay compounds with the best hot air resistance shown by Cloisite 10A (compounds 1c and 1d). Rubber degradation brought about by heat aging is always a concern in any rubber compound
25 because of the corresponding loss of mechanical properties which limits the functional life of the final rubber part. The improved heat resistance provided by nanoclay addition is considered as important asset, extending the life of the rubber compound.

Although the invention has been described in detail in the foregoing for the purpose of illustration, it is to be understood that such detail is solely for that purpose and that variations can be made therein by those skilled in the art without departing from the spirit and scope of the invention except as
5 it may be limited by the claims.